

# DEVELOPMENT OF AN ANALYSIS METHOD FOR TOTAL NONMETHANE VOLATILE ORGANIC CARBON EMISSIONS FROM STATIONARY SOURCES

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## ABSTRACT

The accurate measurement of the total nonmethane volatile organic carbon emissions from stationary sources is critical to characterizing of many industrial processes and for regulating according to the Clean Air Act. Current methods are difficult to use and the ability to do performance audits has been marginal, especially at low concentrations (50 parts per million of carbon, ppmc).

One of the key elements for an ideal measurement technique would be a detector that responds to all classes of organic compounds equally, based on the number of carbon atoms present. A commercially available catalytic flame ionization detector (CFID) has shown promise in this area. Laboratory studies with a CFID were performed to determine the response of compounds with various functional groups. These classes included brominated, chlorinated, nitrogenated, oxygenated, aromatic, and non-aromatic compounds. The response of each compound is compared to the response of an alkane with the same number of carbon atoms. This paper will discuss this phase of the experimental work. Future work with this detector will incorporate an approach for sampling, sample recovery, and field tests for comparison to the EPA Method 25.

## INTRODUCTION

The accurate measurement of the total nonmethane volatile organic carbon emissions from stationary sources is critical to the characterization of many industrial processes. Current methods are difficult to use especially at low concentrations (50 ppmc). One of the key elements for an ideal measurement technique would be a detector that responds to all classes of organic compounds, equally based on the number of carbon atoms present. The flame ionization detector (FID, the detector of choice for most of the analytical methods) responds to unsubstituted alkanes in this manner. However, when functional groups are added or when the structure (aromatic or cyclic) changes, the response no longer follows this pattern. A commercially available catalytic flame ionization detector (CFID) has shown promise in this area.

The CFID uses a ceramic source coated with a nickel/aluminum oxide to act as a combination ignitor, polarizer, and catalytic surface in an H<sub>2</sub>/air flame environment. The CFID ceramic catalyst temperature is controlled through a power supply that is adjustable from 0.0 to 4.0 amperes (amps). Increasing the current to the catalyst raises the source temperature. A balance between the catalyst temperature and the detector temperature is essential to the complete combustion of organic compounds. Generally, the catalyst temperature can be varied from 400 to 800°C, and the detector temperature can be varied between 100 to 400°C.<sup>1</sup>

The detector's performance was evaluated by analyzing organic compounds with various functional groups (halogen, oxygen, nitrogen, and aromatic). Functional groups were evaluated at different currents and fuel ratios until an optimal current and fuel ratio was found that gave a

universal response. Once the optimal conditions were determined, the performance of the CFID was compared to the performance of an FID. The overall performance of the CFID was evaluated by analyzing 61 organic compounds. The response ratio for each compound was compared to the response ratio of straight-chained alkanes. All of the response ratios are based on the number of nanomoles (nmoles) that were injected on column.

## EXPERIMENTAL METHOD

A CFID and power supply available from DETector Engineering & Technology, Inc. (DET) was installed on a Varian 3600 gas chromatograph (GC). The power supply current was variable from 0.0 to 4.0 amps. The FID was a Varian FID installed on a Varian 3400 GC. The analytical column, used for all analyses, was a DB-5, 0.54 millimeter x 30 meter, fused silica capillary column. A PE Nelson 3000 series Chromatography Data System was used for data acquisition and processing.

The detector tower temperature was set at 310°C for all of the experiments. The temperature limit for the column, as indicated by the manufacturer, was 350°C. The operating conditions were well below the limits of the column.

The fuel/air ratio, as recommended by DET for the CFID, was a 1:10 mix of hydrogen and air. To minimize source deterioration, DET recommended that the flow of hydrogen not exceed 25 mL/min and the flow of air not exceed 250 mL/min. The maximum flows were chosen for the initial studies, and a different ratio was later evaluated.

A mix of four aliphatic hydrocarbons was prepared at a concentration of 1.0 millimoles (mmole) each in dichloromethane. This mix was used as the baseline for evaluating the detector response to the number of carbon atoms present. A solution of dichloromethane, trichloromethane, and tetrachloromethane (single carbon chloroalkanes) in nonane was prepared with each compound at 0.12 mmol. The chloroalkane solution was analyzed on the CFID with the current set at 0.0 and on the FID for comparison. The chloroalkane solution was then analyzed on the CFID at six different currents: 0.0, 2.0, 2.4, 2.8, 3.2, and 3.6 amps, to find the optimal current for the chlorinated compounds. A mix of six aliphatic hydrocarbons was prepared at a concentration of 0.013 mmol in dichloromethane.

Different mixtures containing compounds of specific functional groups were then prepared. The standards were prepared at a nominal concentration of 500 µg/mL. An internal standard (IS), nonane, was added to each solution at a concentration of 115 µg/mL. The standards were analyzed at the optimal current, and at a higher current to determine the effects on the different functional groups.

The response factor (RF) for each compound was calculated using equation 1. The response factor to nmol was plotted against the number of carbons in each compound.

$$RF = (\text{Compound area/IS area}) * (1/\text{nmoles of compound injected}) \quad (1)$$

A "least-squares-fit" was applied to the data points from each functional groups with the slope, intercept, and correlation coefficient calculated for each of the generated lines. The linear regression information was compared to the results for the aliphatic hydrocarbons. The number of carbons that each compound deviated from the aliphatic line was calculated using equation 2.

$$\text{No. Carbons Deviated} = \text{No. of carbons in compound} - \frac{[(RF \text{ of compound} - \text{intercept of base line})/(\text{slope of base line})]}{\quad} \quad (2)$$

The average number of deviated carbons was calculated for each class of compounds for comparison to the aliphatic hydrocarbons.

## RESULTS AND DISCUSSION

A mixture of four straight-chained alkanes (heptane, octane, nonane, and decane) was analyzed on the CFID and compared to the FID as a preliminary test of detector linearity. The

CFID was comparable to the FID, with both detectors showing linearity with increasing carbon number for the aliphatic hydrocarbon mix.

Chlorinated compounds were chosen for the initial experiments because of their low response on FID, as compared to alkanes. Single carbon compounds (dichloromethane, trichloromethane, and tetrachloromethane) were selected so that the only difference between the compounds was the number of chlorines present. With 0.0 amps of current applied to the detector, the chloroalkanes responded similarly, on a molar basis, when analyzed on the CFID. When the chloroalkanes were analyzed on the FID, the response decreased as the number of chlorines increased. The chloroalkane standard was then analyzed at 0.0, 2.0, 2.4, 2.8, 3.2, and 3.6 amps to determine the optimal current for this class of compounds. As the current was increased, the sensitivity increased, but the baseline became increasingly noisy. The best compromise between sensitivity, uniform response, and baseline stability was found to be at a current setting of 2.4 amps.

A mixture of six aliphatic hydrocarbons (hexane, heptane, octane, decane, tetradecane, hexadecane) was prepared from stock standards four times and analyzed in duplicate using the CFID with the current set at 2.4 amps (Figure 1). The RFs were averaged and a "least-squares-fit" was applied to the data points (Table I). The aliphatic hydrocarbons responded linearly on the CFID with a correlation coefficient of 0.992, and the resulting line was used as the baseline for comparison with the other compound classes.

Separate mixtures of compounds from five functional groups (aromatic, brominated, chlorinated, nitrogenated, oxygenated) with nonane as the IS were prepared and analyzed at 2.4 amps. The RF for each compound was compared to the RF for the aliphatic hydrocarbons. Some of the compounds could be placed in several of the functional groups, but they were grouped together based on the predominate functional group. Additional studies were performed at higher currents for the aliphatic, aromatic, chlorinated and oxygenated compounds in an attempt to improve linearity and sensitivity.

Figures 1 through 6 provide a graphical representation of the CFID response versus carbon number for the six functional groups studied at 2.4 amps. For comparison purposes, a "least-squares-fit" was performed on each data set that generated a value for the slope and correlation coefficient. The two values for each data set were compared to those generated for the aliphatics compounds, which was used as the target or theoretical situation. The data from the "least-squares-fit" for the aliphatic compounds and the RF calculated for each compound associated with the other functional groups were used to calculate the number of carbon atoms for each compound. This experimentally determined value for the number of carbon atoms was then compared to the actual number of carbon atoms in each compound (Table I).

The plotted slopes for the nitrogenated and oxygenated compounds (Figures 5 and 6) are similar to that for the aliphatic compounds, which indicates that the responses increase with the number of carbon atoms (as expected for normal alkanes). However, the magnitude of the responses was less than that for the aliphatics, making the experimentally determined carbon number for the nitrogenated compounds, on the average, low by approximately 0.5 carbon and the oxygenated compounds low by approximately 1 carbon.

The slopes for the aromatic and brominated (Figures 2 and 3) compounds were greater than that for the aliphatics. This shows that the CFID response increases as carbon numbers increase but at a greater magnitude than for aliphatic compounds. The experimentally determined carbon number for the aromatics was found to be high, on the average, at 0.4 carbons, whereas, the experimental number of carbons for the brominated compounds was found to be equal to the number of actual carbons.

The slope for the chlorinated compounds was less than for the aliphatics, indicating that the CFID response increases as the number of carbons increase, but at a magnitude less than that for the aliphatics. The experimentally determined number of carbons was high, on the average, by 0.4 carbons. The correlation coefficients were all greater than 0.93. This indicates that all of the data points lay on or near the resulting line.

Several functional groups were analyzed at a higher current to possibly improve linearity and sensitivity. Aliphatic, aromatic, oxygenated, and chlorinated compounds were analyzed at 3.2 amps. Table II shows the resulting linear regression data for the compounds that were analyzed. Linearity was not improved with the correlation coefficients less than 0.96. Sensitivity toward increasing

carbon numbers increased slightly for the oxygenated compounds, compared to the slope of the lines at 2.4 amps and 3.2 amps, and the experimentally determined number of carbons, on average, increased by 0.4 carbons. Sensitivity did not increase for the chlorinated compounds, with the slope increasing and the experimentally determined number of carbons, on average, increased to 2 carbons.

The oxygenated compounds were of special interest, since they are a major component of many Method 25 analytes. They showed a reduced response, as compared to the aliphatic hydrocarbons, therefore it was important to closely examine this class of compounds. As noted above, increasing the current did not change the overall response of the compounds. The fuel-gas mixture was changed to 40 mL/min for hydrogen and 250 mL/min for air. The CFID did not behave well at this fuel ratio. The baseline was erratic, and the signal dropped below the baseline after the solvent peak passed through the column. The CFID behaves better at a 1:10 gas ratio; therefore the ratio cannot be changed to achieve better sensitivity towards a functional group.

As a confirmation of the response of the CFID toward the oxygenated compounds, the oxygenated compounds were analyzed with aliphatic hydrocarbons on the CFID at 2.4 amps and the FID. The CFID response to the oxygenated compounds was the same as the FID response. Table III lists the compounds analyzed and the response on the CFID and the FID. The number of carbons deviated from the target aliphatic line was calculated and the results are listed in Table III. The average number of carbons deviated from the target response was -1.25 for both the CFID and the FID.

There were 61 compounds analyzed on the CFID. Figure 6 shows all of the compounds analyzed on the CFID, and Table IV lists all of the compounds that were analyzed in order of increasing response factor. The compounds show that the CFID response increased as the number of carbons increased. The response for the compounds that are showing a low response are only low, on average, by 1 carbon atom.

## CONCLUSIONS

The CFID is a detector that acts as a carbon counter, in that the response to compounds increases linearly as the number of carbons increases. Oxygenated compounds did not respond as well as the other functional groups but did respond linearly with increasing carbon number. For halogenated compounds, the CFID out performed the FID with a response that was unaffected by the number of chlorine atoms and responded linearly with increasing carbon number. The CFID at 2.4 amps results averaged one carbon number or less deviation when compared with aliphatic compounds. The CFID has remained stable after over 6 months of continuous use. The CFID is a versatile detector that is able to overcome some of the selectivity problems of the FID. The CFID appears to be a good choice as a universal detector that may increase the overall detection limit of current stationary source analyses methods.

## DISCLAIMER

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## REFERENCES

1. Theory and Operation of the TID / CFID Detectors, FTD Detector, Remote FID Detector, Tandem TID Detector, FID Detector; DETector Engineering & Technology, Inc., 1991, pp 1-2 - 1-6.

Table I. Linear Regression for Compounds at 2.4 amps.

Functional Group	No. Compounds Analyzed	Slope	Intercept	Corr. Coef.	Avg Deviation From Target (No. Carbons)
Aromatic	7	0.0611	-0.1028	0.9872	0.41
Brominated	3	0.0501	-0.0011	0.9990	0.07
Chlorinated	20	0.0401	0.0461	0.9642	0.40
Aliphatic	6	0.0435	0.0154	0.9964	0.01
Nitrogenated	8	0.0477	-0.0380	0.9771	-0.50
Oxygenated	17	0.0456	-0.0349	0.9711	-0.90

Table II. Linear Regression for Compounds at 3.2 amps.

Functional Group	No. Compounds Analyzed	Slope	Intercept	Corr. Coef.	Avg Deviation From Target (No. Carbons)
Aromatic	7	0.0453	0.0159	0.9284	0.33
Chlorinated	15	0.0328	0.1345	0.8968	1.99
Aliphatic	3	0.0155	0.2447	0.9538	-0.10
Oxygenated	4	0.0490	-0.0293	0.7969	-0.49

Table III. CFID at 2.4 amps vs FID for Oxygenated Compounds.

Compound	RF CFID	RF FID	CFID DEV. CARBONS	FID DEV. CARBONS
4-Methyl-2-Pentanone	0.1482	0.1479	-3.0	-3.0
p-Tolualdehyde	0.3234	0.3291	-0.9	-0.8
2-Butanone	0.1438	0.1457	-1.1	-1.0
Acetone	0.0898	0.0902	-1.3	-1.3
Ethyl Ether	0.1410	0.1480	-1.1	-1.0
Methanol	0.0394	0.0363	-0.5	-0.5
Propanol	0.1114	0.1075	-0.8	-0.9
Ethyl Acetate	0.1253	0.1215	-1.5	-1.6

Table IV. Organic Compounds Analyzed on CFID.

Aliphatic	Aromatic	Brominated	Chlorinated	Nitrogenated	Oxygenated
Hexane	Benzene	Dibromomethane	Methylene chloride	4-Nitrophenol	Methanol
Heptane	Toluene	1,2-Dibromoethane	Chloroform	2,4-Dinitroaniline	n-Propyl Alcohol
Octane	o-Xylene	Bromobenzene	Carbon tetrachloride	2,4-Dinitrotoluene	Acetone
Decane	Ethylbenzene		1,1-Dichloroethylene	4-Nitroaniline	Methyl ethyl ketone
Tetradecane	m-Xylene		1,2-Dichloroethane	1,4-Dinitrobenzene	Ethyl acetate
Hexadecane	p-Xylene		1,1,2-Trichloroethane	2,6-Dinitrotoluene	Ethyl ether
	1,2,4-Trimethylbenzene		1,1,2,2-Tetrachloroethane	1-Nitronaphthalene	2-Butanone
			Trichloroethylene	Diphenylamine	Valeraldehyde
			Tetrachloroethylene		Hexanal
			1,2-Dichloropropane		1-Butanol
			1,2,3-Trichloropropane		Phenol
			Hexachlorocyclopentadiene		4-Methyl-2-pentanone
			2-Chlorophenol		Benzaldehyde
			1,2,4-Trichlorobenzene		p-Tolualdehyde
			Dichlorobenzene		Acetophenone
			4-Chloro-3-methyl-phenol		1-Octanal
			o-Chlorophenol		Isophorone
			1,4-Dichlorobenzene		
			4-Chlorotoluene		
			Chlorobenzene		

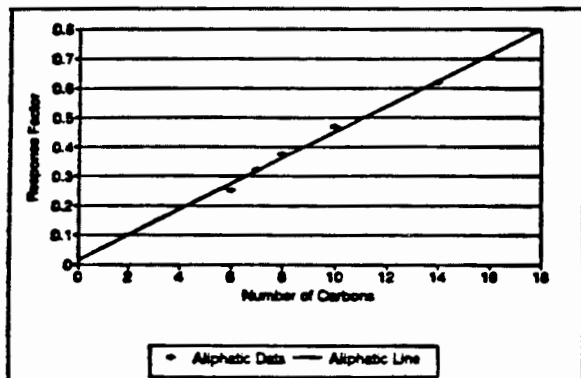


Figure 1. Aliphatics at 2.4 amps.

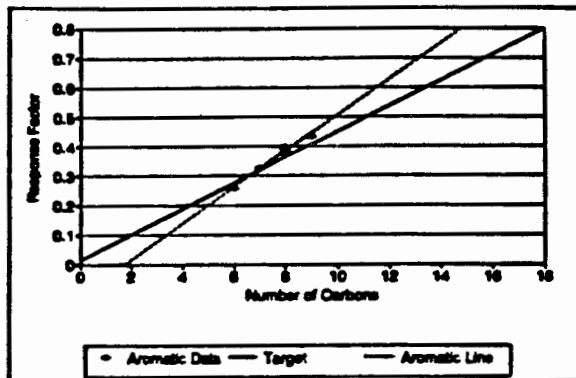


Figure 2. Aromatics at 2.4 amps.

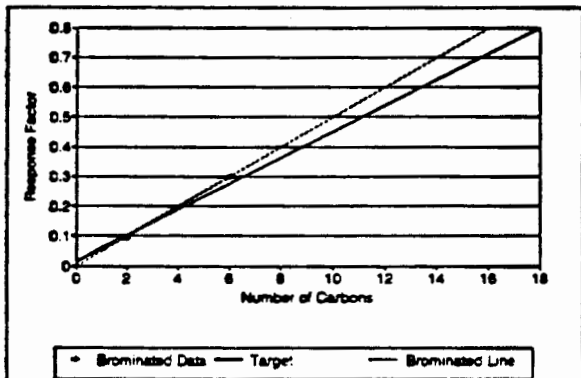


Figure 3. Brominated at 2.4 amps.

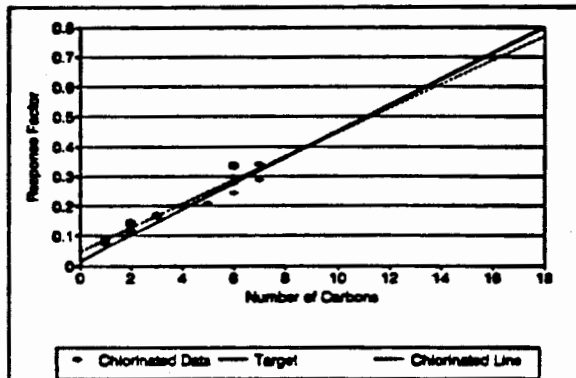


Figure 4. Chlorinated at 2.4 amps.

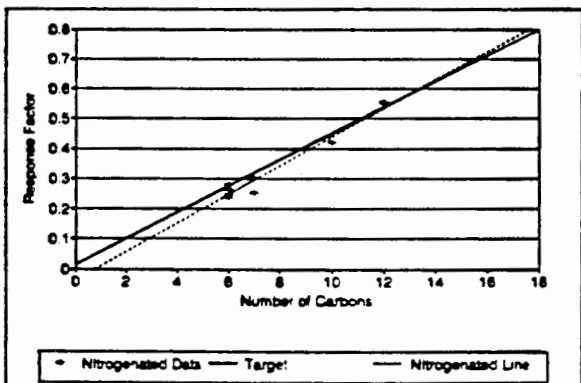


Figure 5. Nitrogenated at 2.4 amps.

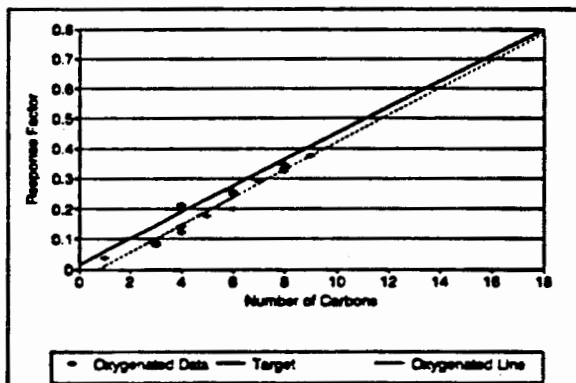


Figure 6. Oxygenated at 2.4 amps.

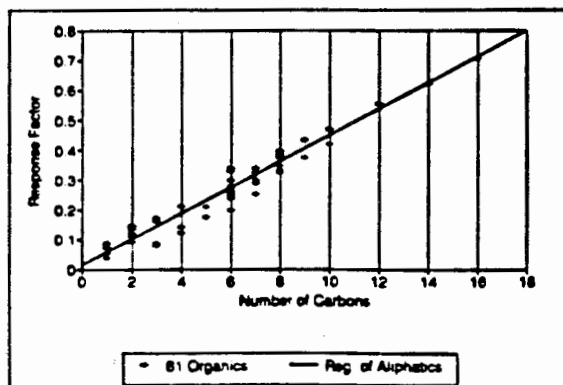


Figure 7. 61 Organics at 2.4 amps.

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